

# Reactions of Fatty Materials With Oxygen. VIII.<sup>1</sup> Cis-Trans Isomerization During Autoxidation of Methyl Oleate<sup>2,2a</sup>

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THE initial stages of autoxidation of olefins are immensely important in investigating the mechanisms of this reaction. Ultra-violet spectrophotometric examination of certain non-conjugated polyolefins (5, 15) during the early stages of oxidation has given much useful information on the type and amount of oxygen-induced conjugation. With monoolefins, unfortunately, ultra-violet spectrophotometric examination of the oxidation mixture during the early stages is of little value because the starting materials and the oxidation products do not show any absorption bands within the operating range of conventional laboratory spectrophotometers. The ease with which oxygen causes changes in double bond systems however suggested that an examination of autoxidation mixtures should be made with the object of determining whether an oxygen-induced cis-trans isomerization occurs, particularly during the initial stages of oxidation.

Positive evidence for the occurrence or non-occurrence of oxygen-induced cis-trans isomerization is of considerable theoretical importance for many reasons, several of which are given. a) Although both isomeric 9,10-dihydroxystearic acids (m.p. 95° and 130°) can be isolated (about 5-15% yields) from methyl oleate or oleic acid autoxidation mixtures, the high-melting isomer predominates (32), whether the autoxidation mixture contains metal-salt catalysts or is irradiated with ultra-violet. High-melting 9,10-dihydroxystearic acid can be obtained by cis hydroxylation (31) of oleic acid or methyl oleate (direct addition of two hydroxyl groups formed possibly from hydroperoxides by radical decomposition) or from elaidic acid or methyl elaidate (formed by isomerization of oleic acid or methyl oleate) by epoxidation (cis addition) followed by hydrolysis (inversion occurs). b) The 9,10-epoxystearic acid isolable (about 5-15% yields) from methyl oleate or oleic acid autoxidations is the low-melting (trans) isomer (10, 11). This isomer can presumably only be obtained by epoxidation (cis addition) of methyl elaidate or elaidic acid (formed by isomerization of oleic acid or methyl oleate). c) In the autoxidation of other cis-monoolefins the  $\alpha$ -glycol obtained mainly is the isomer comparable in configuration to that obtained from the autoxidation of methyl oleate or oleic acid (see a) above). It is obvious that several reactions are probably going on simultaneously in the same autoxidation system.

The development of infrared spectrophotometric techniques within the past few years has provided a method for the detection and quantitative determination of trans monoolefins in the presence of large amounts of cis isomer (1, 2, 16, 17, 19, 20, 27, 29, 35). This method is based on the fact that trans mono-

olefins show an intense absorption band in the infrared region at a wavelength of about 10.3-10.4 microns whereas cis monoolefins do not. So far as we know, there is no other method available for the detection of small quantities of trans monoolefins in mixtures.

Methyl oleate irradiated with ultra-violet light has been autoxidized at 35°. Samples were withdrawn at intervals and infrared absorption spectra were determined on the liquids from 2 to 15 microns. In the present investigation we were mainly interested in interpretation of the spectra in the region between 10.2 and 10.5 microns. In subsequent papers we will report extensions and amplifications of this work, namely, interpretation of other regions of the infrared spectrum, spectra of solutions of oxidation reaction mixtures, autoxidation of methyl elaidate, and autoxidation of methyl oleate at other temperatures.

Infrared spectrophotometric examination of oxidation reaction mixtures has also been used by Gamble and Barnett (18), Honn, Bezman, and Daubert (21), and Dugan, Beadle, and Henick (9). Gamble and Barnett studied methyl eleostearate and pigmented methyl oleate and glyceryl trieleostearate whereas the last two groups of workers studied autoxidizing linseed oil and methyl linoleate, respectively. The major emphasis in these investigations was on the regions of the infrared spectrum in which the hydroxyl group (2.9 microns) and the carbonyl group (5.7 to 6.0 microns) absorb.

## Experimental

**Starting Material.** Methyl oleate, b.p. 180° at 4 mm., was prepared by the acid-catalyzed esterification of pure oleic acid obtained from olive oil fatty acids by multiple low temperature fractional crystallization and vacuum distillation (7, 33). The material contained about 3% of saturated esters but was free of polyunsaturated (6) and trans (29, 35) components.

**Oxidation Procedure.** Methyl oleate was placed in a three-neck flask made of highly polished, solarized quartz, and the flask and contents were irradiated with two 125-watt unfiltered, quartz-mercury ultra-violet lamps placed eight inches from the flask. Tank oxygen at the rate of 20 liters per hour was passed through the methyl oleate by means of fritted discs, the temperature of the reaction ranging from 31-39° C. (average 35°C.). Samples were removed at intervals and stored in tightly-stoppered bottles in the dark at 0° to minus 25°C. until the infrared spectra were obtained.

**Infrared Spectra.** A Beckman IR-2 infrared spectrophotometer equipped with an automatic slit-width controlling mechanism was employed (28). Relatively thick liquid cells were employed (0.0104 and 0.0116 cm.) so that groups present in small amounts during the early stages of oxidation would have a better chance of being detected. The oxidation samples were examined as liquids rather than in solution. Figure 1 shows infrared absorption spectra (percentage of transmission against wavelength) from 2 to 15 mi-

<sup>1</sup> The previous paper in this series is reference 30.

<sup>2</sup> Presented at the Fall Meeting of the American Oil Chemists' Society in San Francisco, Calif., Sept. 26-28, 1950.

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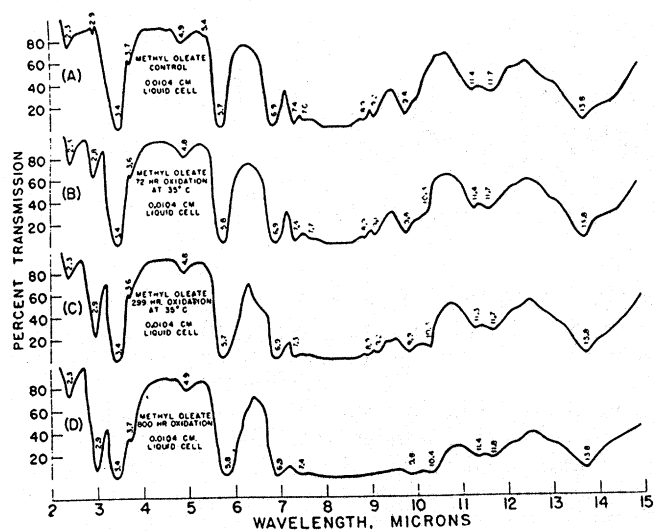


Fig. 1.

rons of unoxidized methyl oleate and methyl oleate oxidized for various times. The extra absorption around 6-7 microns in curves C and D is caused by water vapor. Figure 2 is a plot of differences in absorbance indices (optical density, or absorbance, divided by cell thickness in cm.) between the unoxidized and oxidized methyl oleate against wavelength from 10.20 to 10.45 microns, for various oxidation times. Figure 3 is a plot of the ordinate at 10.31 microns of each curve of Figure 2 against time in hours. Figure 4 is a plot, similar to Figure 2, of absorbance index relative to unoxidized methyl oleate after the oxidized samples had been reduced with sodium bisulfite to destroy peroxides (22).

**Peroxide Oxygen.** For comparison and assessing the extent of oxidation, peroxide oxygen values calculated as moles of peroxide oxygen per 100 g. of substrate are listed in Table I. These were deter-

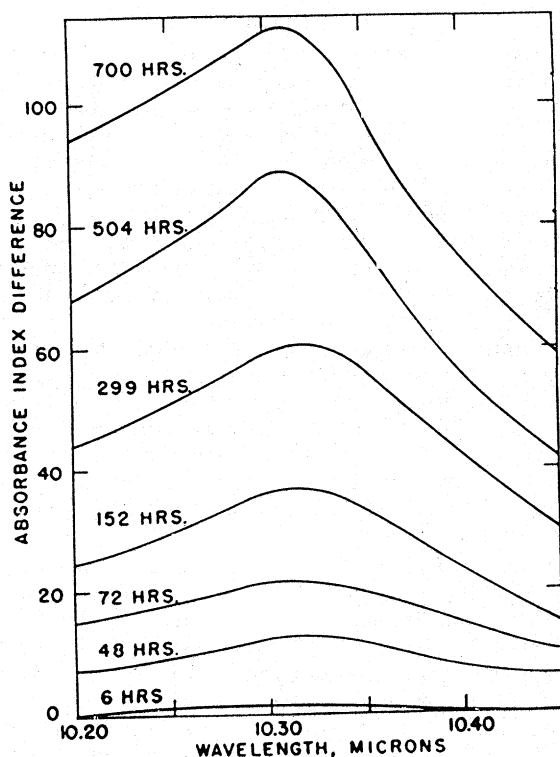


Fig. 2. Plot of difference between absorbance indices of oxidized and unoxidized methyl oleate against wave length.

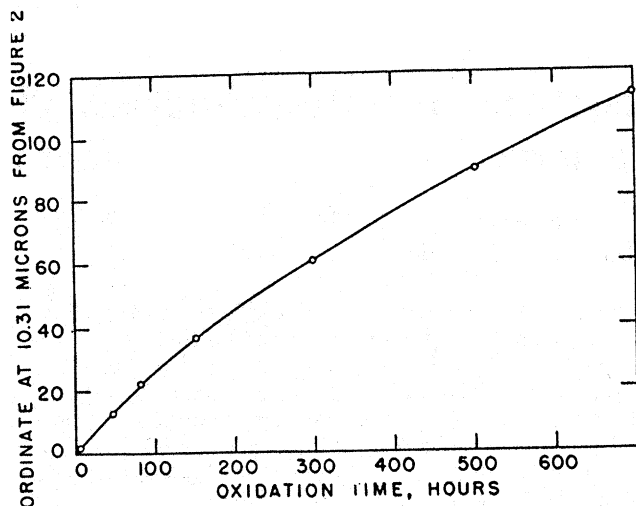


Fig. 3. Plot of difference between absorbance indices of oxidized and unoxidized methyl oleate at 10.31 microns against oxidation time.

mined by Wheeler's method (36) except that oxygen was excluded and 15 minutes' reaction time was employed. Figure 5 is a plot of the ordinate at 10.31 microns of each curve of Figure 2 against moles of peroxide oxygen per 100 grams of substrate.

Complete chemical analytical studies of the oxidation described in this paper, as well as oxidations conducted at higher temperatures, will be reported in another paper.

TABLE I  
Peroxide Oxygen Values in Ultra-Violet Light-Catalyzed Autoxidation of Methyl Oleate at 35°C.

Oxidation Time, Hrs.	Peroxide Oxygen, <sup>1</sup> Moles per 100 g. of substrate
0.....	0
6.....	0.002
24.....	.008
48.....	.014
72.....	.024
98.....	.029
123.....	.040
152.....	.048
200.....	.052
299.....	.067
408.....	.069
504.....	.088
600.....	.104
700.....	.096
800.....	.111

<sup>1</sup> Peroxide oxygen in moles per 100 g. of substrate is calculated by dividing the percentage of active oxygen, determined by Wheeler's (36) method, by 16. The calculated value for pure methyl oleate hydroperoxide is 0.305 mole of peroxide oxygen per 100 grams.

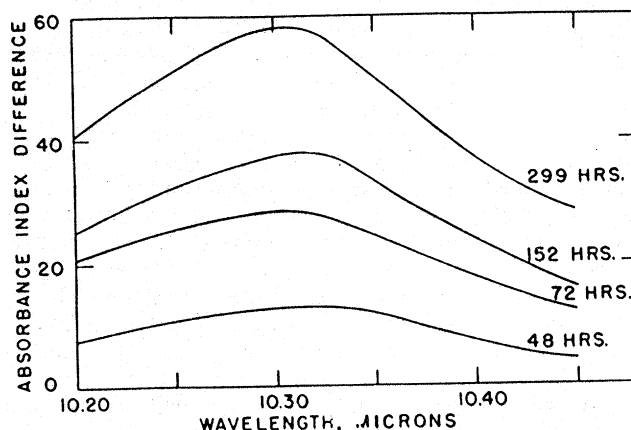


Fig. 4. Plot of difference between absorbance indices of oxidized-reduced and unoxidized methyl oleate against wave length.

## Results and Discussion

The infrared spectra of Figure 1 reveal two absorption bands of special interest. As the oxidation proceeds, absorption increases at 2.8 to 2.9 microns (caused by hydroxyl stretching vibrations) and at about 10.31 microns (caused by bending vibrations of C-H groups attached to a trans double bond). The increase in the hydroxyl absorption band roughly parallels the build-up in total peroxidic and other hydroxyl oxygen and is in agreement with data in other publications (9, 21). The increase in absorption in the 10.31-micron region is not as pronounced as that in the 2.9-micron region because of overlapping by the strong band at 9.8 microns, and special handling is required to bring out the change that occurs.

The increase in absorption in the 10.2- to 10.5-micron region is shown in Figure 2 in which the differences between absorbance indices of the oxidized and unoxidized methyl oleate are plotted against wavelength. This method of plotting subtracts out the background due to the strong methyl ester absorption at 9.8 microns and allows the weaker band, due to trans unsaturation, to be seen more clearly. It is evident that an absorption maximum is developing at 10.31 microns as the oxidation proceeds. This is shown even more clearly by plotting the ordinate at 10.31 microns of each curve of Figure 2 against the oxidation time (Figure 3). To eliminate the possibility that peroxide groups are contributing to or causing this absorption band, oxidation samples reduced with sodium bisulfite were also examined spectrophotometrically in this region. The data are similarly plotted in Figure 4. At comparable oxidation times the curves of Figures 2 and 4 are substantially the same. Thus there is no diminution in intensity of absorption in this wavelength region by elimination of peroxide. It is reasonable to conclude therefore that a cis-trans isomerization is occurring during the initial stages of autooxidation of methyl oleate and continues to occur and build up, certainly to 700 hours.

Two control experiments were also performed. A sample of methyl oleate was irradiated for 168 hours at 35°C. with the same intensity of ultra-violet radiation as the oxidation samples previously described, but through which oxygen-free nitrogen was being passed. Another sample of methyl oleate was treated with oxygen for 432 hours at 35°C., but in complete darkness. Both of these control samples gave infrared curves which differed negligibly from that of untreated methyl oleate. These two samples developed peroxide oxygen contents of 0.00 and 0.02%, respectively. Evidently, actively oxidizing conditions are required to produce the cis-trans isomerization since neither oxygen nor ultra-violet irradiation alone at 35°C. produces the reaction. Other aspects of this interesting phenomenon are being actively pursued.

From Figure 5 it is evident that the development of trans material parallels the formation of peroxides up to 300 hours (0.067 mole of peroxide oxygen per 100 g. of substrate). The deviation from linearity in the later stages of oxidation is to be expected since peroxide decomposition is probably increasing. Although we have no way of calculating the content of trans material exactly, an approximate calculation can be made from the ordinates at 10.31 microns of Figure 2, but employing the absorbancy index (ex-

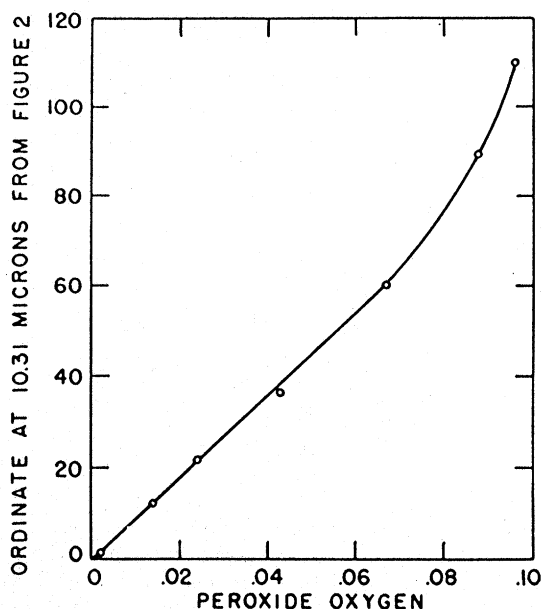


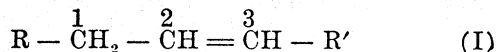
Fig. 5. Plot of difference between absorbance indices of oxidized and unoxidized methyl oleate at 10.31 microns against peroxide oxygen in mol/100 gram of substrate.

inction coefficient) data obtained by Swern, Knight, Shreve, and Heether (29, 35) at 10.36 microns for methyl elaidate. It is then found that the molal concentration of trans material is roughly 90% of the molal concentration of peroxide oxygen at all times up to 300 hours. A more accurate calculation is not justified because the absorbancy index of the trans compound(s) in the oxidation mixtures may not be the same as that of methyl elaidate.

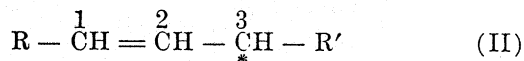
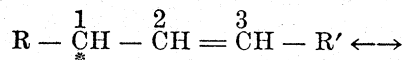
These data suggest that most, if not all, of the peroxides produced during the autooxidation of methyl oleate, at least up to 300 hours at 35°C., are trans peroxides and not methyl oleate peroxides, as had been previously supposed. It is suggested that the peroxides obtained in the autooxidation of methyl oleate be called (collectively) methyl octadecenoate peroxides until more definitive information regarding their actual structures is available.

### Mechanisms of Isomerization

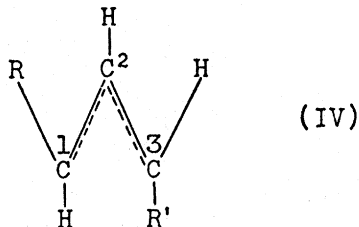
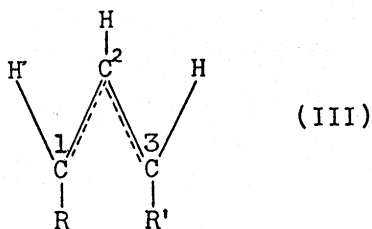
According to recent work, mainly of Farmer and co-workers (12, 13, 14, 15) and Bolland (4), the central feature of the mechanism of autooxidation of



during the early stages is the radical



whose electronic structure is that of a resonance hybrid. Since maximum resonance energy is attained when all three carbon atoms and their three hydrogen atoms lie in the same plane, and since the configuration having lowest energy is that of maximum resonance energy, the resonance hybrid should not be capable of free rotation. Radical II should exist in one or the other of two isomeric forms,

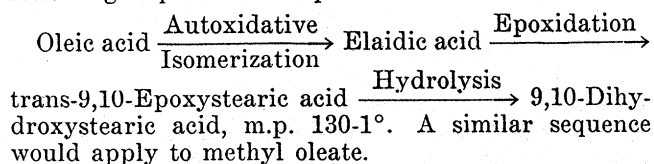


both of which could be produced by removing a hydrogen atom from I, since free rotation is possible about the single bond between carbon atoms 1 and 2 before the removal of the hydrogen. The relative proportions of III and IV would be determined presumably by the same type of steric factors which determine the relative amounts of cis and trans structures in any isomerization reaction.

In the formation of the hydroperoxide, addition of oxygen to carbon atom 1 in either III or IV would give a cis hydroperoxide. Addition to carbon atom 3 of III would also give a cis hydroperoxide, but addition to carbon atom 3 of IV would give a trans hydroperoxide. The infrared evidence suggests that the majority of the radicals take configuration IV, add oxygen at carbon atom 3, and become a trans hydroperoxide which could be a mixture mainly of methyl 9-hydroperoxido-trans-10-octadecenoate and methyl 10-hydroperoxido-trans-8-octadecenoate.

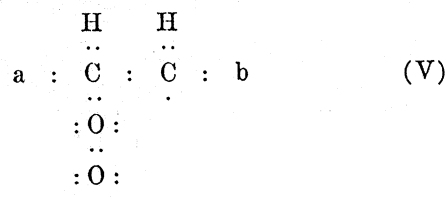
Although the above explanation seems reasonable with the amount of infrared and other data available, the following alternative explanations should also be considered:

a) The trans compounds may not be peroxidic but may form at the same rate as the peroxides. Since we have shown by the control experiments described earlier in the paper that if peroxides are not formed, trans components are also not formed, it can be concluded possibly that the peroxides or radicals derived from them are cis-trans isomerization catalysts for methyl oleate. The fact that trans-9,10-epoxystearic acid can be isolated in 5-15% yield from oleic acid oxidations (10, 11) suggests that elaidic acid must be a precursor since epoxidation proceeds in one step without inversion. The formation of trans-9,10-epoxystearic acid and high-melting 9,10-dihydroxystearic acid can be formulated therefore as occurring in the following sequence of steps:



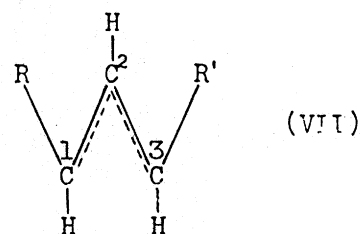
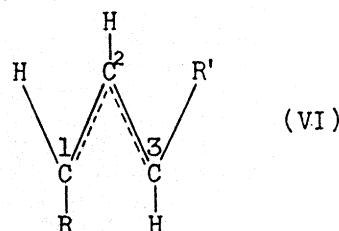
b) Reversible addition of oxygen to the double bond may occur. It has been suggested by earlier workers (12, 13, 23, 24, 25, 26, 34), on the basis of energy considerations and for other reasons, that the

initial intermediate in olefin autoxidations is the biradical V, in which oxygen adds to the double bond.



Although V forms to only a limited extent, it initiates  $\alpha$ -methylenic reactions which represent the main chain-propagating and autoxidation steps. While the oxygen is attached, the biradical can undergo free rotation. Detachment of the oxygen would give a mixture of cis and trans isomers, the more stable trans form predominating. This possible mechanism for cis-trans isomerization, involving transitory attachment and then detachment of the isomerizing agent, is analogous to that proposed as a general mechanism for the isomerization of olefins by the usual catalysts (3, 8, 23). Since double bonds shift during autoxidation, mixtures of cis and trans isomers in which the double bond is not in the original position should also be obtained.

c) The addition of oxygen to radicals III and IV may be reversible. While the oxygen is on carbon atom 3, free rotation would be possible about the 2,3 bond, and detachment of the oxygen would lead to two additional isomeric forms (VI and VII).



Reacquisition of a proton would then give a mixture of methyl oleate and elaidate as well as cis and trans methyl 8- and 10-octadecenoates. Attachment and detachment of oxygen to carbon atom 1 would not yield any isomers which have not already been discussed.

d) The radicals III and IV may be capable of some degree of rotation so that the isomerization takes place without the addition of oxygen to them. Subsequent addition of oxygen or reacquisition of a proton would give all of the hydroperoxides and octadecenoates mentioned previously.

It should be emphasized that autooxidative isomerization is only one of numerous reactions which are occurring during autoxidation.

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## Summary

Methyl oleate irradiated with ultra-violet light has been autoxidized at 35° and the reaction has been followed by means of the infrared spectrophotometer. During the extremely early stages of autoxidation and continuing up to at least 700 hours, a cis-trans isomerization induced by oxygen is one of the reactions which occurs.

The data suggest that most, if not all, of the peroxides produced during the autoxidation of methyl oleate, at least up to 300 hours, are trans peroxides and not methyl oleate peroxides, as had been previously supposed. A mechanism for the formation of trans peroxides from allylic free radicals is proposed.

Mechanisms are also proposed for the formation of non-peroxidic trans materials during autoxidation. These could explain the formation of trans-9,10-epoxystearic acid and high melting 9,10-dihydroxystearic acid from autoxidizing oleic acid.

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